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Comparison of *Parthenium argentatum* and *Hevea brasiliensis* rubber: Effect of non-rubber constituents on rubber intrinsic properties.

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ABSTRACT

Natural rubber (NR) is an indispensable polymer used to manufacture industrial products and has many exceptional features that makes it as yet irreplaceable by synthetic rubber. Currently, almost all NR used in commerce comes from the hevea tree (Hevea brasiliensis). However, to meet the increasing demand for NR, guayule (Parthenium argentatum) has emerged on the market as a sustainable commercial source of high quality rubber. Guayule rubber (GR) has similarities to hevea rubber but also has unique properties. For example, it was found to be malleable at extremely cold temperatures. We aim to understand causes of this malleability to tap this potential for aerospace, cryogenic sealing, and other low temperature applications.

Non-rubber constituents play an important role in NR intrinsic properties. We conducted research on GR malleability by comparing the effect of non rubber constituents, such as protein, lipid and resin. Firstly, a film casting method was developed to obtain rubber films with a uniform thickness. Secondly, the physical properties were tested by dynamic mechanical analysis (DMA). Acetone solubles (lipids and resin) were found to soften the rubber and behave as plasticizers. Furthermore, removal of the rubber particle membrane (proteins and lipids) was found to affect the tensile properties of the films.

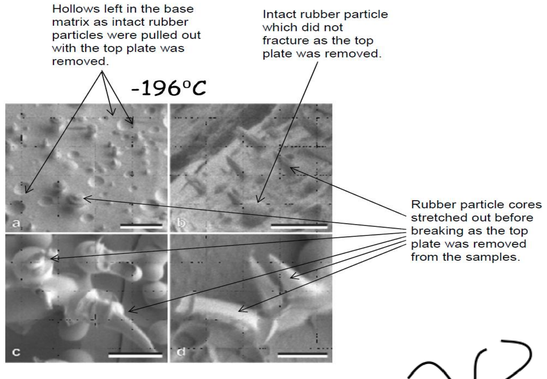
INTRODUCTION

Natural rubber has outstanding tensile properties and good crack growth resistance, which originates from its ability to crystallize upon elongation[1].

This crystallizability upon elongation, known as *strain-induced crystallisation*, is derived from **non-rubber constituents** present in NR, the regularity of isoprene units in the *cis*-1,4 configuration[2] and the natrually occuring network (Fig.2) Guayule is an alternative source of commercial rubber which has several versatilities: it does not cause Type I and Type IV allergy problems for people already sensitized to Hevea latex[3] and, unlike other NR, guayule rubber particles were found to be still malleable at cryogenic temperature[4]

(-196°C) (Fig.1).

This malleability difference could be due to the qualitative and quantitative variations of the non-rubber constituents. We have compared the mechanical properties of Hevea rubber (**NR**), low molecular weight Hevea rubber (**LMwNR**), guayule rubber (**GNR**) and membrane removed guayule rubber (**MRGNR**).



a,b, *in situ*; c,Tris buffer; d, 0.2% ammonia

Figure 1: Guayule rubber particles photographed after top freeze-fracture plates was removed to induce a fracture plane[4]. Key: a,b particles are in situ in bark parenchyma (bars = 3µm); c, particles purified from the plant in Tris buffer (bar = 2µm); d, particles purified in 0.2% ammonium hydroxide (bar = 1µm).

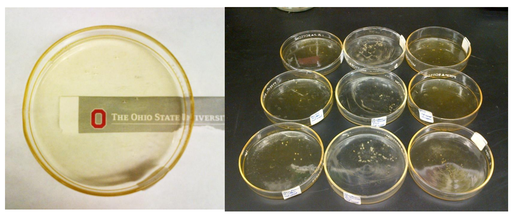


Figure 3: films cast from rubber-$CHCl_3$ mixture.

METHODS

MRGNR was prepared with chemical and enzymatic treatments of **GNR** latex. **LMwNR** was obtained from the soluble fraction of **NR** in hexane after 3h of mixing. Rubbers with acetone-soluble constituents removed were prepared by washing 3.5 g of rubber sample with 2 × 30 ml acetone for 48h at room temperature.

Film casting method: 3.5 g of rubber was dissolved in ~50 ml $CHCl_3$. The mixture was shaken for 24h, centrifuged at 3800 rpm for 10 min at 20°C. Then the films were cast in glass petri dishes (Fig.3). The thickness of the films obtained was ~ 0.4 mm. Films of 7 × 5.3 × 0.4 mm dimension were analyzed by DMA.

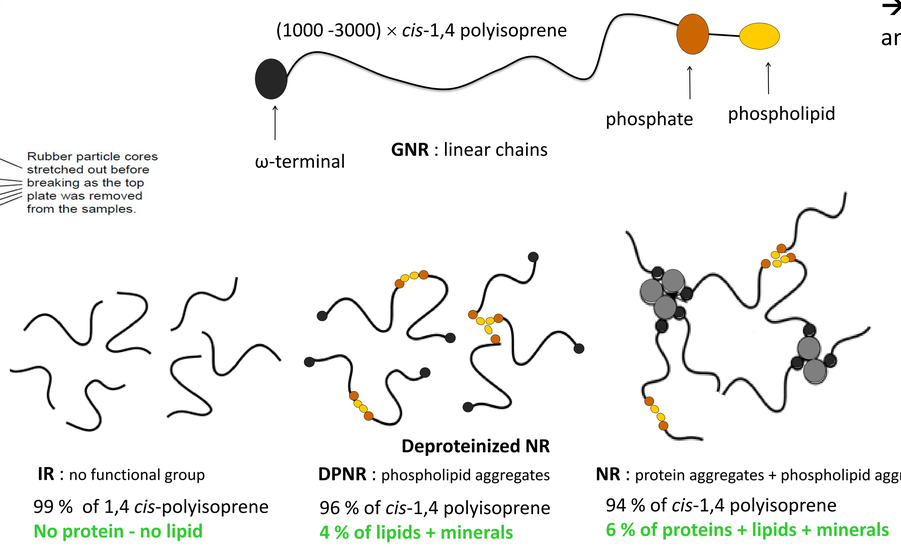


Figure 2: participation of non-rubber constituents in branch-points. The network created by branch-points strengthens the material. Adapted from reference [5].

sample	acetone extract weight for 3.5 g rubber sample (g)	resin % in the sample
GNR	0.42	12
MRGNR	0.27	7.7
NR	0.10	2.9
LMwNR	0.23	6.5

Table 1: amount of acetone soluble recovery after extraction. acetone fraction is mainly composed of resin.

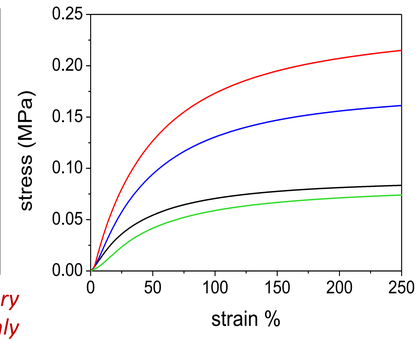


Figure 5: stress-strain plot of rubber films. 10% error margin for all curves.

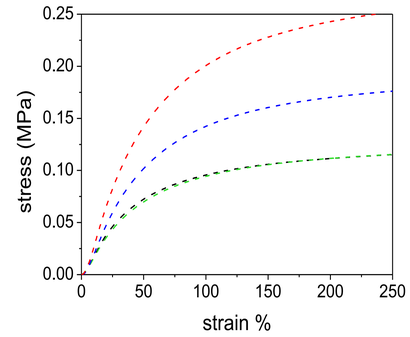


Figure 6: stress-strain plot of rubber films with acetone soluble constituents extracted. 10% error margin for all curves .

RESULTS AND DISCUSSION

→ **NR**, **GNR**, and **MRGNR** were found to have similar glass transition temperatures (T_g). These materials contain rubber and non-rubber constituents which must be contributing to the T_g because the T_g of the **GNR** particle cores is clearly much lower than seen here (Fig.1). The stress-strain plot of rubber films (Fig. 5) shows a stiffness decreasing sequence of **NR**> **LMwNR**> **GNR**> **MRGNR**. The weight average molar mass (M_w) is estimated at 1.7 ×10^6 g mol^{-1} for **NR**[6], at 0.3 ×10^5 -2.2 ×10^5 g.mol^{-1} for **LMwNR**[7] and at 1.33×10^6 g mol^{-1} for **GNR**[6].

→ It is well known that the longer and more branched a polymer chain is, the more entanglement can occur and consequently, the stiffer and stronger the native polymer is (Fig.2). Thus, it is not surprising that **NR** is stiffer than **LMwNR**.

→ **LMwNR** still appears to have higher modulus than **GNR**. Even assuming that **GNR** and **LMwNR** have the similar M_w still **LMwNR** is a stronger material. This difference can be assigned to the higher amount of branch points in **LMwNR** than in **GNR**.

→ **MRGNR** films appear to be softer than **GNR** films: the removal of proteins and phospholipids destroys the naturally occurring network (Fig.2), resulting in a decrease in tensile properties[8].

→ An overall increase in the modulus is observed for all acetone-extracted (AE) samples. Acetone soluble compounds include resin, a complex mixture of terpenoids, glycerides, lipids, and pigments[9]. Since lipids behave like plasticizers, their removal enhances the strength of the material. Still **GNR-AE** is softer than **LMwNR-AE** and **NR-AE**. This can be explained by the higher amount of proteins in HR compared to **GNR,** which participate in the branch point formation.

→ **MRGNR** rubber contains a higher amount of acetone soluble compounds than **LMwNR** and **NR** (Table 1).

→ After removal of the membrane of **GNR** particles, lipids and resins still appear to be present in the rubber core, and may play a role in the cryomalleable property observed (Fig. 1).

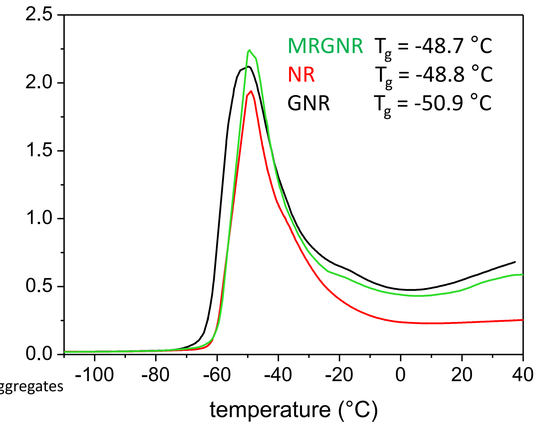


Figure 4: glass transition of MRGNR, GNR and NR measured with DMA.

CONCLUSION

The higher amount of acetone soluble compounds in **MRGNR** than in **NR** and **LMwNR** seems to be responsible of the softness and the malleability of **MRGNR** films. This result also indicates that there is still ~7.7% of lipids, resin and other acetone soluble compounds remaining in the guayule rubber core. Further experiments have to be conducted at low temperature to verify there role in cryomalleability.

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